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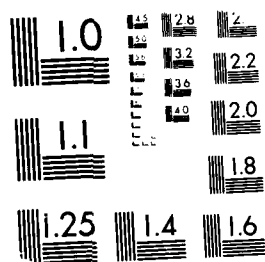   ESTABLISHMENT HARWELL (ENGLAND) C C NAISH ET AL
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Variability with surface condition of potentials measured on reinforced concrete structures

C C Naish and R F A Carney

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VARIABILITY WITH SURFACE CONDITION OF POTENTIALS

MEASURED ON REINFURCED CONCRF E STRUCTURES

C C Naisl and R F A Carney

ABSTRACT

This paper presents some observations on the variability of measurements obtained during a "potential mapping" survey of a concrete structure. The results are discussed in terms of Evan's diagrams and conclusions drawn on the cause of the effects observed.

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Introduction

This paper presents some observations on the variability of measurements obtained during a "potential mapping" survey of a concrete wall. Very large discrepancies were observed during trials of a new potential logging instrument based on a portable micro-computer (Epson HX-20). The brief series of measurements reported here were carried out to find the cause of these discrepancies. The results are discussed in terms of Evans's diagrams and conclusions drawn on the cause of the effects observed.

Experimental

The criteria used to determine the state of reinforcing steel in concrete by "potential mapping" are the value and distribution of the apparent half cell potential of the steel as measured on the surface of the concrete. These measurements are normally made by connecting the steel to the +ve side of a high impedance DVM, and the -ve side to a saturated calomel electrode which is in contact with the concrete surface via a suitable conducting electrolyte solution and a porous wooden plug (Figure 1).

In the tests described here, measurements were made on a grid pattern over one wall of a small exposed reinforced concrete structure. At each point on the grid the surface of the concrete was chipped away to remove the cement rich layer and any carbonated concrete. This was done before the first measurements, and all subsequent measurements were made at these points without further chipping or abrasion. Before each measurement the grid point was wetted by painting it with 0.1M NaOH solution and contact to the half cell was made by placing the wooden plug on the prepared surface. Wetting and measurements were done in blocks of ten, and good stable readings were obtained in this way.

The microcomputer system (Thompson Electrochem Ltd.) comprised an HX-20 Epson microcomputer linked to a high impedance (> $10^{11}\Omega$) analogue voltage measuring circuit via an RS-232 interface. The complete system was battery powered from a 12V 1.8 Amp-hour sealed lead acid battery.

Initial readings were taken one afternoon immediately after heavy rain. The following day when weather conditions were dry, sunny and with a strong wind, potential measurements on a block of 10 points using a Fluke 806A multimeter in its high impedance mode ($10^{10}\Omega$) were found to be much less negative than those obtained the previous day. This same block was then re-measured using the micro-computer system and this sequence (multimeter/micro-computer) was repeated several times at intervals of several minutes (see results) with the grid point being re-wetted with 0.1M NaOH as they appeared to dry out. A further series of readings was taken using the multimeter on the following morning after overnight rain.

Results

Results are presented in Table 1 and in Figures 2 and 3. It is clear that the results obtained after heavy rain were much more electronegative, particularly the first results which were taken shortly after driving rain had thoroughly wetted the wall. With one exception (point 6/18) the results taken on the 'dry' wall showed a progressively more negative half cell potential with time. On further examination point 6/18 was found to be contaminated by a waxy substance which probably accounts for its anomalous behaviour. Similar results, exhibiting a movement to lower potentials on wetting, have been noted both in laboratory[1] and field[2] experiments by other workers.

Discussion

The steady trends with time of readings from alternate instruments mean that these differences cannot be accounted for by instrument variations However, it is hardly possible that the true half cell potential of the steel beneath at least 40mm of concrete could change so dramatically in so short a time and it is concluded the change in apparent half cell potential at the surface of the concrete must be due to changes in the resistivity of the outer few mm of concrete.

We believe the potential changes observed above can be explained by the following analysis, which is general in applicability, and that they have considerable consequences in the application of the potential mapping technique and its use to define degrees of corrosion attack.

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The following analysis will use potential-current curves (Evans'
diagrams) to illustrate the behaviour of steel in concrete, and a brief
introduction to this approach may be appropriate. First let us examine
some simpler hypothetical situations. Consider a steel electrode in
concrete with equal, distinct anodic and cathodic areas, these areas having
respective potentials E_a and E_c relative to some reference electrode (E_c
would be positive of E_a in formal convention). If the concrete had
infinite electrical resistance a diagram such as Figure 4 would apply.
(The potentials could not actually be measured because of the insulating
concrete.) If the resistance of the electrolytic medium becomes finite
then a current flows from the cathode to the anode with the reinforcement
bar completing the electrical circuit. As in any galvanic cell, (e.g. a
battery) when a current flows, polarization occurs; the potentials of the
anode and cathode move towards one another relative to their open-circuit
(zero current) values.

For the case of equal area electrodes with negligible electrolyte
(solution) resistance the polarization is governed by the kinetics of the
charge-transfer reactions across the electrochemical interface (the
solution-metal boundary), and these polarization characteristics (I-V
curves or Tafel slopes) are plotted on an Evans diagram in Figure 5. This
diagram indicates a corrosion potential, E_{corr} and a corrosion current,
i_{corr} defined by the point at which the curves meet. The potential in such
a situation can be measured by connecting a high-impedance digital
voltmeter between a reference electrode in the solution and the metal
reinforcement bar. The current cannot be directly measured as the anode
and cathode cannot be separated. However, should it be possible to
localize them and place a zero-resistance ammeter between them then the
current observed would be i_{corr}.

To discuss the behaviour of steel in concrete, two changes must be
made to the above. The first is the form of the cathodic polarization
characteristic (Tafel relationship) and the second is to take account of
the large, but finite resistance of concrete.

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Any electrochemical oxidation (anodic) reaction e.g. iron dissolution:

$$Fe \rightarrow Fe^{2} + 2e^{-} \qquad (1)$$
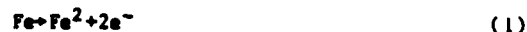
must be balanced by a reduction (cathodic) reaction, otherwise a charge build-up would occur and any reaction would stop. In the case of steel corroding in concrete this reaction is nearly always oxygen reduction:

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \qquad (2)$$

Hence overall:

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2 \qquad (3)$$

Reaction (2) is kinetically slow (it has a small exchange current) and is limited, not by the rate of charge transfer across the interface but by the rate at which dissolved oxygen gas diffuses to the interface (it is a diffusion limited reaction). Such a cathodic reaction has a polarization characteristic that tends towards a maximum current which is almost potential independent, leading to large polarizations at quite small current levels. By contrast polarization of the anodic reaction is extremely small for the same currents.

The resistance of the concrete further limits the current which can flow between the anode and the cathode, which is reduced from i_{corr} to i'_{corr} by introducing an 'iR drop' (according to Ohm's law $= V = i_{corr}R$), see Figure 6.

It can be seen from Figure 6 we no longer have a single value of E_{corr}. Some of the potential between the anode and cathode is being dropped by the current flow through the concrete. If the concrete is of uniform resistivity then the potential dropped can be related to the distance moved along the surface; the concrete surface can be treated as a potentiometer and various voltages tapped-off at distances along its surface. This is the basis of potential mapping: The potential variations

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seen at the surface are caused by the flow of the corrosion current through
the concrete and are hence a function of its resistance. Near to the
cathode a cathodic, positive potential will be observed, whilst near to the
anode, the potential will be an anodic, negative potential, but it is
important to note that the potentials are a property of the current flow in
the concrete and are not the actual potentials of the anode and cathode.

It is possible to explain the movements in potential with wetting and
drying cycles using the Evans diagram approach in terms of changes in the
surface resistivity of the concrete when it is wet or dry. The
current-voltage flux lines along a two-dimensional section of reinforcement
are shown in Figure 7. This assumes constant concrete resistivity. If the
surface is wetted it becomes of a lower resistance, relatively more current
flows through the surface layer, and the current flux (and hence potential
gradients) are altered. The situation is illustrated in Figure 8, which
shows that movements in the potentials measured along the concrete surface
(potentiometer), because of the nature of the two polarization
characteristics, is almost totally in a negative direction. Hence when the
surface is wetted the current moves from i_{corr} to i'_{corr} and the points
being measured move by ΔE_c and ΔE_a where $\Delta E_c >> \Delta E_a$.

Furthermore, an important implication of the above analysis is that
the actual rate of corrosion, indicated by i_{corr} and i'_{corr}, is indeed
increased when the concrete surface is wetted and that significantly
changes can occur on a very short timescale. This, of course, also implies
that misleading information can be obtained if potentials are measured on
surfaces pre-treated by wetting and emphasises the need to carry out
potential mapping surveys under typical environmental and surface
conditions if they were to reflect the true state of reinforcement
corrosion. Wetting and drying cycles can well be appreciated to be the
worst situation for concrete reinforcement corrosion: near-surface wetting
quickly decreases the effective concrete resistance, allowing i_{corr} to
increase without effectively restricting the oxygen flow (as would be the
case for a water saturated concrete). The oxygen flow will be restricted
after some delay but the onset of a drying cycle will most likely pre-empt
this and rapidly replenish the oxygen.

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Conclusions

These results and the following discussion reinforce the opinion that the resistivity of the concrete and its variation with depth beneath the surface must be taken into account if surface potential values are to be properly evaluated and conclusions drawn from them. Work towards this end is presently in progress at Harwell.

Acknowledgement

References

1. Hope, B.B., Ip, A.K. and Manning, D.G., Cement and Concrete Research, 15, pp 525-534 (1985).

2. P. Vassie (Personal Communication).

Table 1   Potential-Time Variations

Instrument used, date and time

| Grid No	Epson DAY 1 1500 hrs	Fluke DAY 2 1356 hrs	Epson DAY 2 1401 hrs	Fluke DAY 2 1405 hrs	Epson DAY 2 1418 hrs	Fluke DAY 2 1430 hrs	Epson DAY 2 1433 hrs	Fluke DAY 3 1030 hrs
6/16	-133	33	-12	-46	-69	-71	-74	-109
6/17	-155	-14	-39	-68	-89	-95	-99	-120
6/18	-161	-125	-130	-129	-131	-130	-131	-115
6/19	-224	-112	-137	-151	-171	-173	-176	-183
6/20	-228	-146	-144	-166	-171	-181	-182	-197
7/16	-118	45	0	-29	-45	-50	-56	-99
7/17	-139	-6	-57	-78	-89	-93	-97	-122
7/18	-165	-91	-110	-116	-136	-131	-135	-138
7/19	-222	-131	-150	-158	-176	-183	-180	-192
7/20	-200	-111	-109	-120	-132	-147	-151	-178
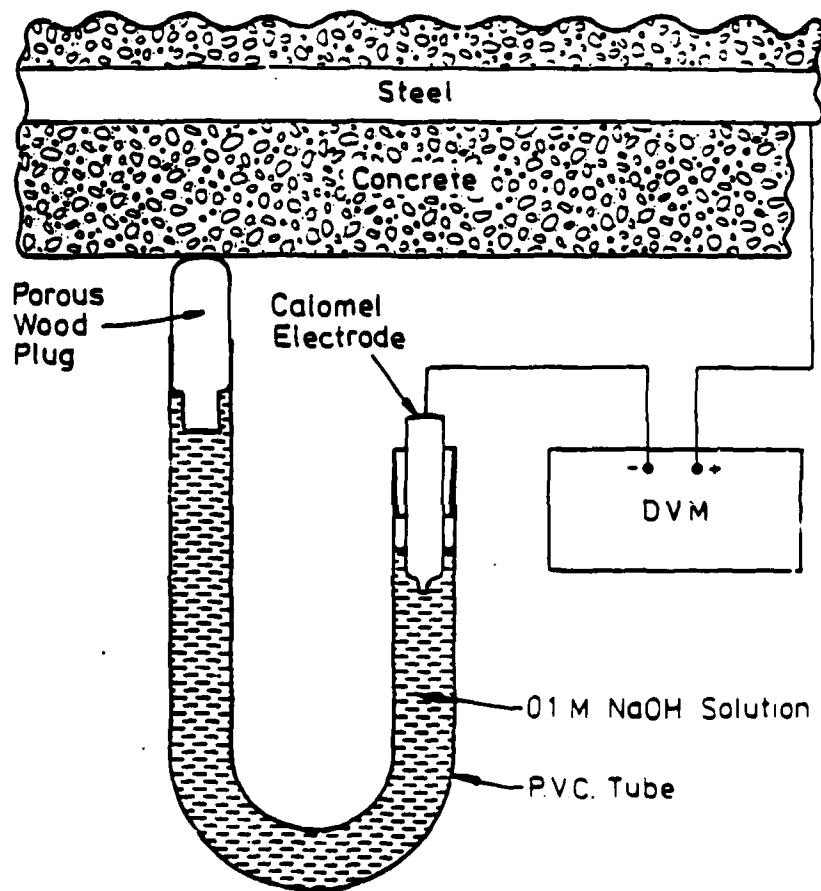
FIG.1 EQUIPMENT USED TO MEASURE APPARENT
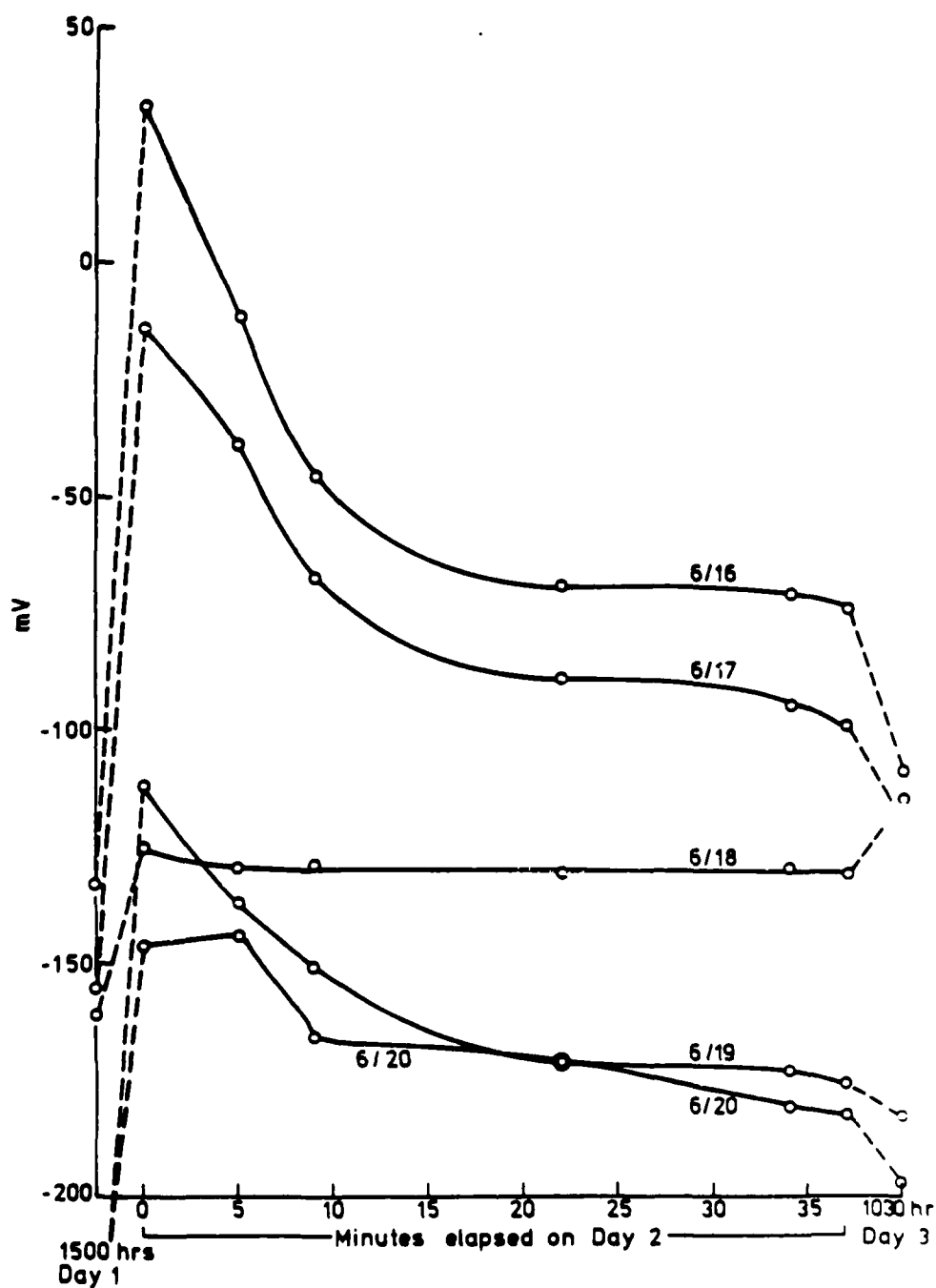HALF-CELL POTENTIALS AT THE SURFACE
OF REINFORCED CONCRETE.

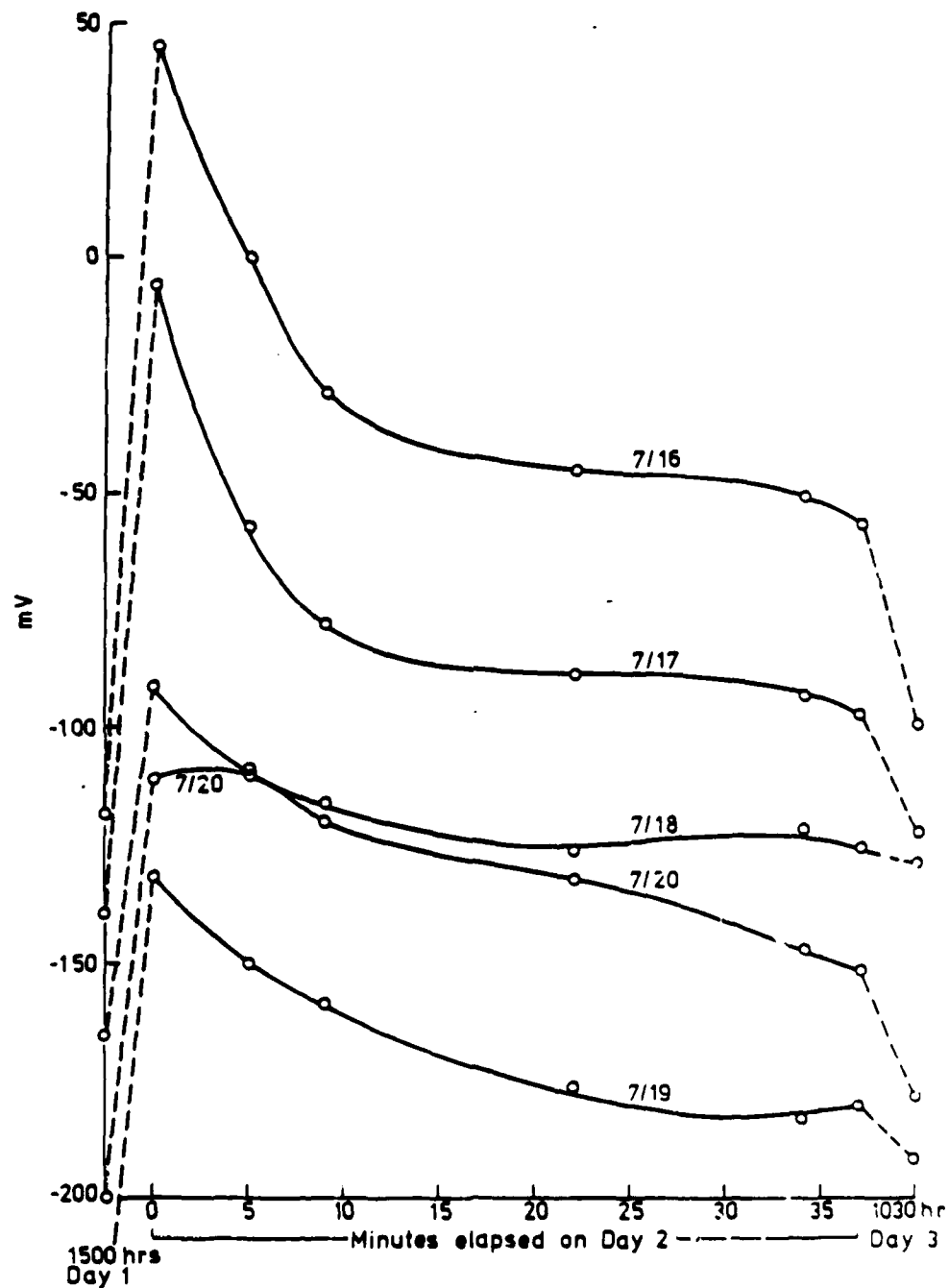FIG. 2. POTENTIAL-TIME VARIATION
(MAPPING GRID ROW 6 POINTS 16-20)

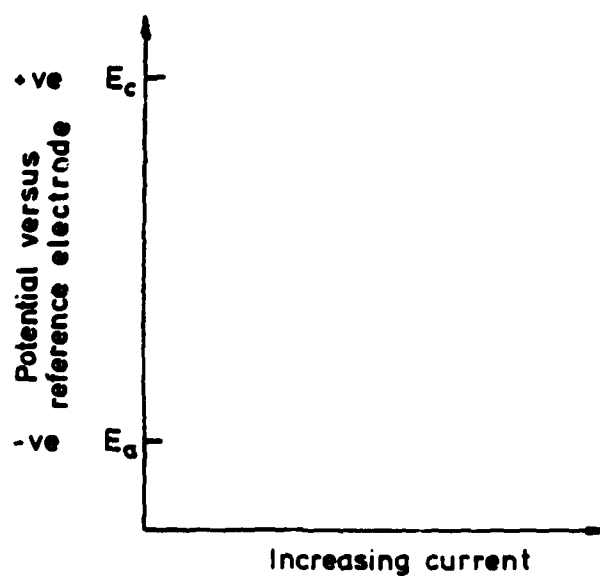FIG. 3. POTENTIAL - TIME VARIATION
(MAPPING GRID ROW 7 POINTS 16 - 20)

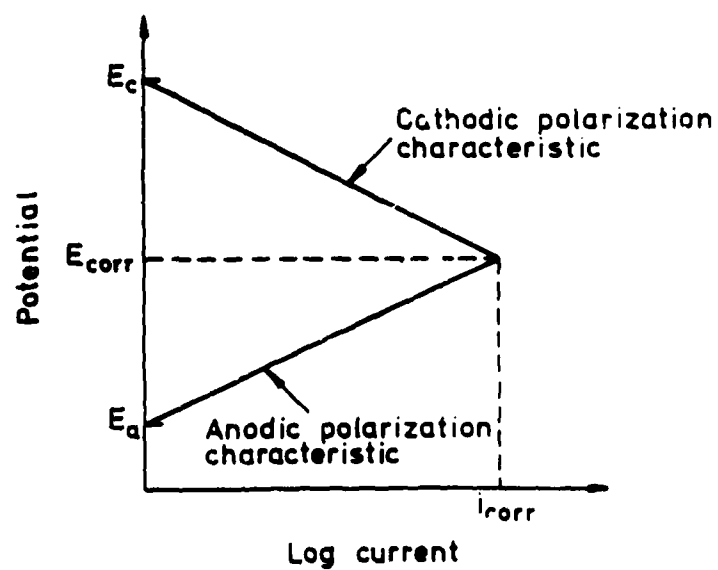**FIG.4.EVAN'S DIAGRAM REPRESENTATION OF ANODE AND CATHODE OPEN CIRCUIT POTENTIALS**

FIG.5.EVAN'S DIAGRAM FOR SYSTEM WITH SIMILAR ANODE AND CATHODE POLARIZATION CHARACTERISTICS
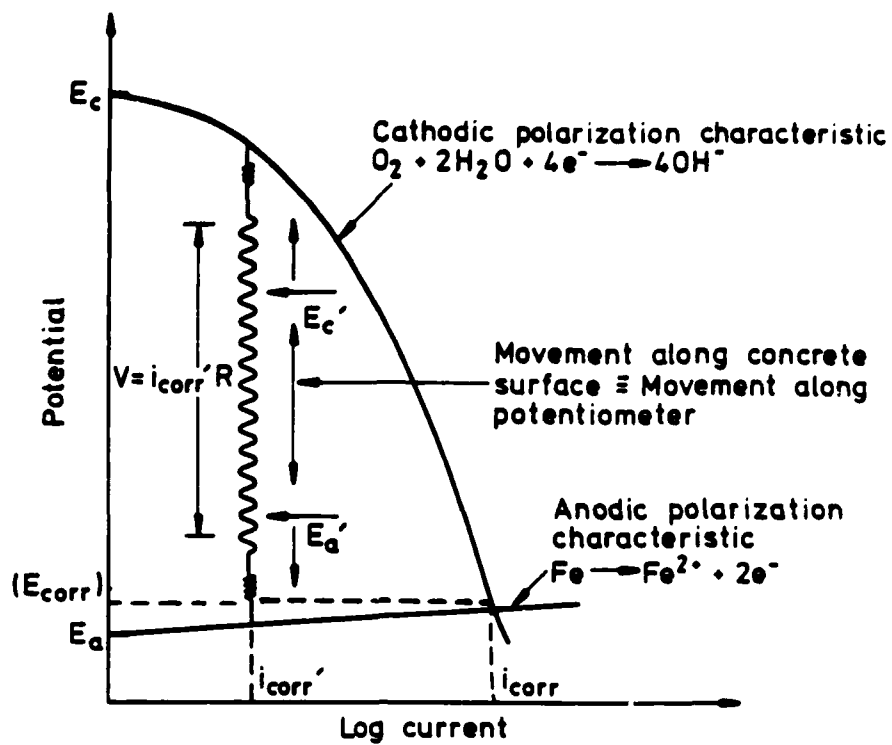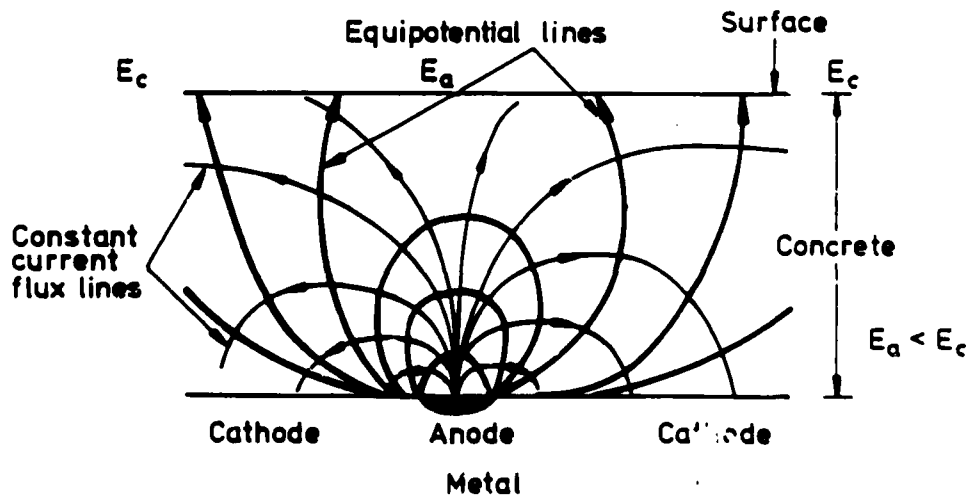
FIG.6. EVAN'S DIAGRAM FOR CORRODING STEEL IN CONCRETE

In the figure, labels include:

- E_c
- Cathodic polarization characteristic $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$
- E_c'
- Movement along concrete surface ≡ Movement along potentiometer
- $V = i_{corr}' R$
- E_a'
- Anodic polarization characteristic $Fe \longrightarrow Fe^{2+} + 2e^-$
- (E_{corr})
- E_a
- i_{corr}'
- i_{corr}
- Potential
- Log current

FIG.7. CURRENT AND POTENTIAL DISTRIBUTION IN CONCRETE NEAR ANODIC CORROSION SITE

Labels include:

- Equipotential lines
- Surface
- E_c
- E_a
- E_c
- Constant current flux lines
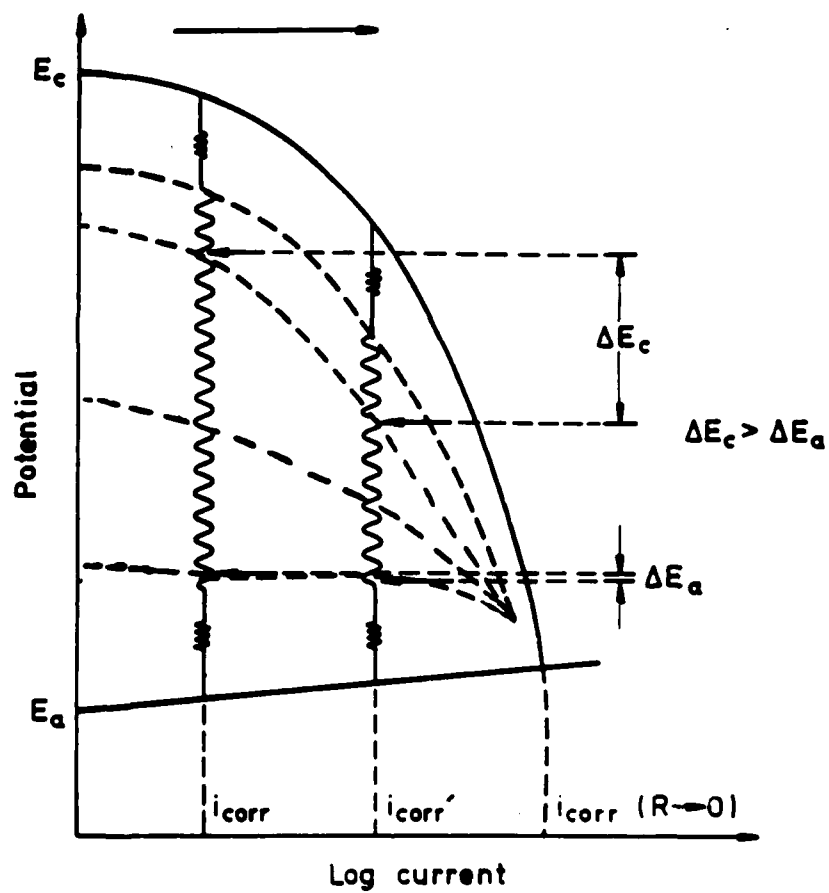- Concrete
- $E_a < E_c$
- Cathode
- Anode
- Cathode
- Metal

FIG.8.EFFECT OF SURFACE WETTING ON MEASURED POTENTIALS
EFFECT OF WETTING : i_{corr} ⟶ i_{corr}'

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